2010 NRL REVIEW

POWER SYNERGY

NAVAL RESEARCH LABORATORY

Washington, DC

Plasma Processing of Ion Energy-sensitive Materials

S.G. Walton,[1] E.H. Lock,[1] M. Baraket,[1] D.R. Boris,[1] R.F. Fernsler,[1] S.H. North,[2] C.R. Taitt,[2] J.T. Robinson,[3] F.K. Perkins,[3] and P.E. Sheehan[4]
[1]*Plasma Physics Division*
[2]*Center for Bio/Molecular Science and Engineering*
[3]*Electronics Science and Technology Division*
[4]*Chemistry Division*

Plasma Processing: Plasmas are a critical tool for the production and modification of materials. These partially ionized gases comprising electrons and positive ions can create or modify large areas with precision down to the nanoscale. Consequently, plasmas have been the semiconductor industry's tool of choice to produce the complex circuitry found in the electronic devices we take for granted. Every plasma has its own profile of reactive species including electrons, ions, excited neutrals, reactive neutral fragments (radicals), and photons. This profile depends considerably on the background gas and can be adjusted precisely. By adjusting this profile, the plasma will remove material, deposit material, or change the chemical makeup of the surface to which it is exposed. Despite a string of successes, serious concerns remain over the use of plasmas in producing and modifying materials used in next-generation electronic, sensing, and energy applications. More specifically, ions with large kinetic energies can produce unwanted effects. For polymers, ion-induced surface roughness can render the material unusable, and in the case of monolayer films like graphene, etching must be avoided.

The plasma processing system developed in NRL's Plasma Physics Division averts these issues because of its ability to deliver ions with very low kinetic energies (Fig. 9). To understand this, one must recognize that most plasmas are sustained by applying electric fields. The applied field couples mainly to the electrons, increasing their energy so that some fraction of the population is energetic enough to ionize the gas. While the electrons are energetic, the ions remain at or near the background gas temperature. In order to prevent the more mobile electrons from leaving, the plasma self-organizes to maintain a positive potential such that electron losses are reduced. Nearly all of this potential arises at the plasma-substrate interface, and so positive ions impacting the substrate arrive with energies well in excess of the electrons. Our approach to plasma generation uses a high-energy electron beam to ionize, excite, and dissociate the background gas. Because electric fields are not required, the plasma electrons have very little energy and so the plasma potential is small as well. In fact, ions arrive at the surfaces with energies of only a few eV, a value that is at or below the bond strength of polymeric materials and graphene. We have successfully functionalized polymer substrates of interest in biothreat detection and diagnostic technologies and treated graphene for electronics and sensing applications without damaging the material.

Chemical Functionalization of Microtitre Plates: With colleagues in the Center for Bio/Molecular Science and Engineering, we have developed a method for chemically functionalizing commercial, polystyrene microtitre plates to facilitate biomolecule immobilization. The multi-well microtitre plate is a standard

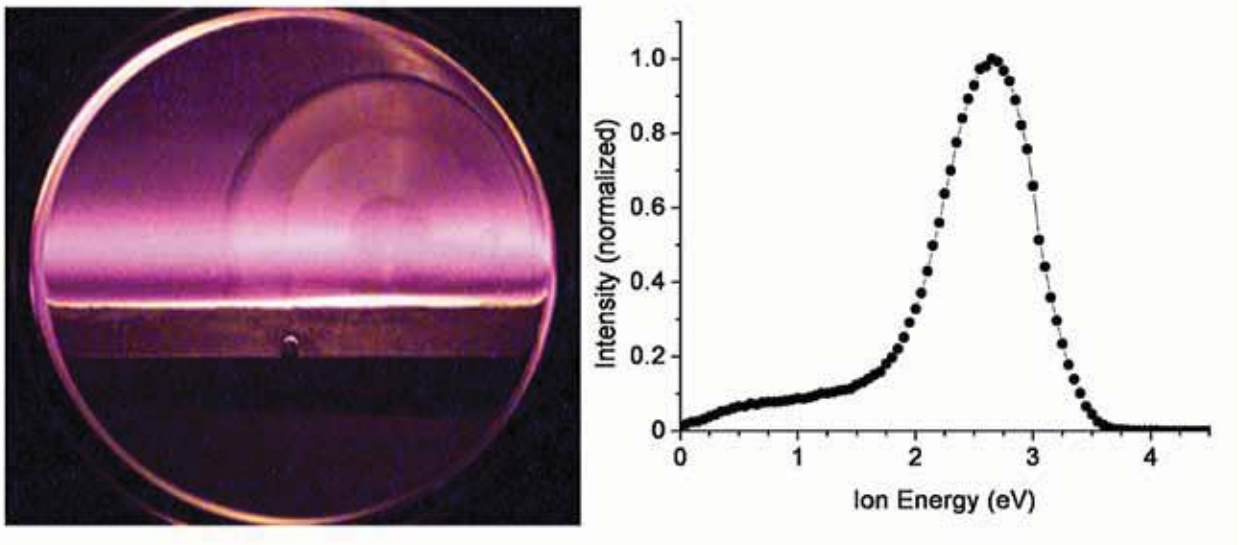

FIGURE 9
NRL's plasma processing system (left) and an ion energy distribution measured at an adjacent processing stage (right). The range of ion energies is below the bond strength of many materials and is a critical feature in the success of the system.

tool used for the development of diagnostic tests and other biological detection schemes. Depending on the target agent, specific "capture" biomolecules are immobilized on the plate surface. While nonspecific adsorption is the most commonly used method for immobilization of proteins, many biomolecules do not retain their enzymatic or binding activities when immobilized in this fashion. Specifically, covalent immobilization allows for a stable and oriented display of these biomolecules. Using our plasma processing system, we introduce chemical functionalities to the plate surfaces, which allow for virtually any type of covalent attachment chemistry without changing the surface morphology. In Fig. 10, we demonstrate differential binding properties of a bacterial biomarker, lipopolysaccharide (LPS), to a variety of antimicrobial peptides (AMPs) immobilized onto plate surfaces that have been treated with plasma (bottom) and those that have not (top). Although the example of Fig. 10 is specific to oxygen, the plasma-based approach is flexible and allows us to introduce a variety of chemical moieties for covalent attachment.

Chemical Functionalization of Graphene: Graphene is a single monolayer of sp^2 bonded carbon, with superlative electrical, mechanical, and thermal properties. However, to increase the range of potential graphene-based applications, precise control over surface functionalities is required. With colleagues in the Chemistry and Electronics Science and Technology Divisions, we have developed an approach that can decorate the surface of graphene with various functional groups without adversely disrupting the graphene honeycomb structure. Figure 11 shows chemical and structural characteristics before and after adding oxygen functional groups. The oxidized graphene has distinct chemical signatures associated with the addition of oxygen as well as a significantly increased D-peak, indicating the transformation from sp^2 to sp^3 carbon. However, the sp^2 carbon and the graphitic-induced G band remain. Importantly, after high-temperature annealing to remove the functionalities, the pretreatment characteristics are recovered, indicating little or no damage to the graphene structure as a result of the treatment. Here again, the

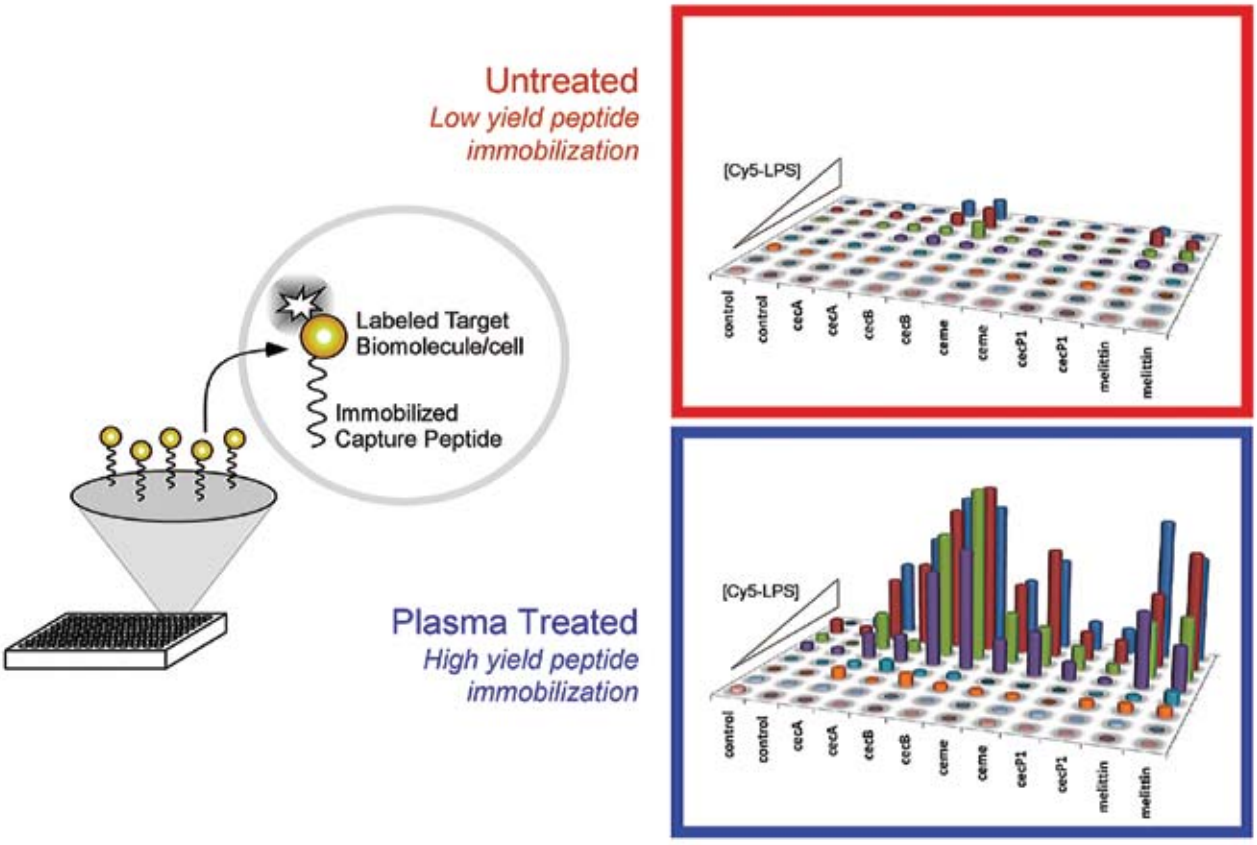

FIGURE 10
Fluorescence from untreated (top) and plasma treated (bottom) microtitre plates indicating the binding of a fluorescently labeled bacterial biomarker, lipopolysaccharide (LPS), to a variety of antimicrobial peptides. Plasma treatment introduces chemical moieties that promote the covalent immobilization of peptides, thereby increasing the LPS capture yield and the associated signal strength by up to 40 times compared to the untreated plates.

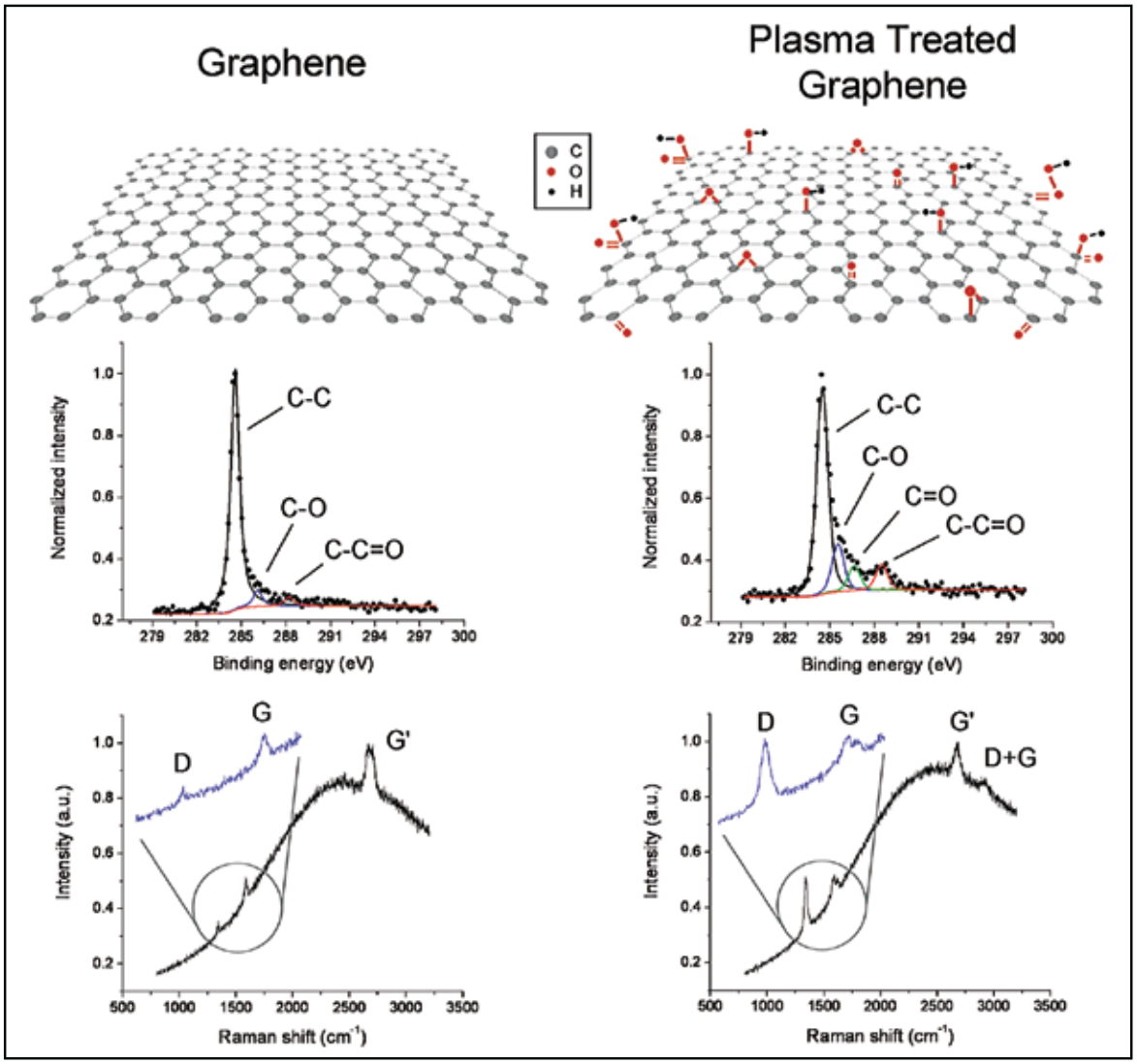

FIGURE 11
A representation of graphene functionalization (top) along with supporting surface diagnostics. X-ray photoelectron spectroscopy (XPS) measurements (middle) show an increase in the oxygen functionalities bound to carbon after exposure to an argon/oxygen plasma. The presence of those species alters the carbon bond structure, as indicated by the increase in the D band signal in the Raman spectrum (bottom).

system's flexibility enables us to tailor the functional group by simply changing the operating gas mixture.

[Sponsored by NRL/ONR and DTRA]

Standoff Detection of Trace Explosive Residues by Resonant Infrared Photothermal Imaging

C. Kendziora,[1] R.A. McGill,[1] R. Furstenberg,[1] M. Papantonakis,[1] V. Nguyen,[1] G. Hubler,[1] and J. Stepnowski[2]
[1]*Materials Science and Technology Division*
[2]*Nova Research Inc.*

Counter-IED Motivation: Motivated by improvised explosive device (IED) and homeland security concerns, explosives detection is a critical research area for the Navy, the Department of Defense (DoD), and the Department of Homeland Security (DHS). An emerging thrust is to potentially replace point detection of trace residues (which requires physical contact) with standoff capability from a safe distance. Ideally, a standoff technique should be safe to use around people, nondestructive, selective, rapid, and adaptable to new types of threats. NRL's Materials Science and Technology Division has demonstrated a novel resonant infrared (IR) photothermal approach that has the potential to meet these goals. In this technique,